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Hydrogen Sensing Characteristics of a Quartz Oscillator

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1. Introduction

A variety of hydrogen sensing technologies have been developed, which mainly involve detection of hydrogen leaked into air and represent key technologies for realization of the “hydrogen society” (Hübert T. et al., 2011). These sensors can be classified into those using chemical sensing and those using physical sensing. Here, chemical sensing is defined as technologies in which chemical reactions with hydrogen are essential. On the other hand, physical sensing is defined as methods other than chemical sensing.

Most conventional hydrogen sensing methods belong to the chemical sensing category. Heat obtained by combustion of hydrogen, which results from the reaction with oxygen, is used for catalytic combustion type hydrogen sensors (Gentry S. J. and Jones T. A., 1986; Han C.-H. et al., 2007; Jones M. G. and Nevell T. G., 1989; Katti V. R. et al., 2002). This heat produced by combustion is transformed into electrical energy using thermoelectric materials, such as Si, SiGe, SnO₂, Pt/Al₂O₃, Pt/activated carbon fiber cloth, and BaCe_{0.95}Y_{0.05}O₃- δ (BCY), in thermoelectric sensors (Mcaleer J. F. et al., 1985; Nishibori M. et al., 2007; Nishibori M. et al., 2010; Qiu F. B. et al., 2003; Röder-Roith U. et al., 2011; Shin W. et al., 2001; Zhang J. S. et al., 2007). Changes in the resistivity and surface conductivity on the oxide semiconductor induced by the reaction between surface oxygen and hydrogen detects hydrogen in oxide semiconductor sensors (Lundstrom K. I. et al., 1975). Generally, these conventional chemical sensors have extremely low detection limits for hydrogen on the order of several parts per million. However, these chemical sensing methods frequently require thermal energy to enhance the chemical reactions for detection, and therefore, are not safe because of heat generation. In addition, their response times are normally on the order of seconds because rates of chemical reactions for sensing are slow and accompanied with a slow rate of heat translation. Moreover, they cannot identify concentrations of leaked hydrogen over 10 vol%. Other noble chemical sensing methods are those using field effect transistors, which

measure threshold voltages affected by reactions between hydrogen and oxygen on the surface (Lundstrom I. et al., 1975)

Physical hydrogen sensing methods defined in this chapter do not include chemical reactions of hydrogen. One representative technique is thermal conductive sensing, making use of the high thermal conductivity of hydrogen (Hale J. et al., 1992; Simon I. and Arndt M., 2002). Optical sensing of hydrogen optically detects changes associated with hydrogen exposure, such as volume expansion, alterations in refractive index, and optical absorption (Butler M. A., 1984). Surface acoustic wave sensing detects hydrogen by measuring the acoustic properties of surface waves induced by hydrogen adsorption (Jakubik W. P. et al., 2002). These physical sensing methods have difficulty in detecting low hydrogen concentrations on the order of parts per million. On the other hand, physical sensing tends to have a quick response, probably because the sensing methods are independent of chemical reactions and thermal energy transfer.

Hydrogen sensing using quartz oscillators is a physical sensing method. Energy is transferred to the quartz oscillator from collision with gas molecules when exposed to a gas. As the energy depends on pressure, viscosity, and molecular weight of the gas, output can be obtained related to these properties of the investigated gas (Kokubun K. et al., 1984). Hydrogen leakage and hydrogen concentration can then be measured using this output. The principles underlying hydrogen sensing are described in detail in the following section.

We have applied this sensing method to measure the partial pressure of binary gas mixtures because viscosity and molecular weight, which can be measured by the quartz oscillator, are only dependent on the partial pressures of each gas in the mixture. For example, the partial pressures of ozone and oxygen in their gas mixture at 100 kPa can be measured with sensitivity of 0.2 kPa (Kurokawa A. et al., 2004). For hydrogen and silane gas mixtures, which are the source gases of thin silicon solar cell materials, the partial pressures of each gas can be measured with the sensitivity of several % for 133-1,333 Pa (Suzuki A. and Nonaka H., 2008). Hydrogen concentration in air can also be derived by an identical procedure, as discussed later.

As hydrogen sensing with the quartz oscillator is classified as a physical sensing method, it has merits of fast response and recovery times and non-consumption of the measured gas. In addition, hydrogen sensing with a quartz oscillator has a number of other advantages. This sensing method works effectively at room temperature and does not require any external energy to enhance the detection efficiency, except that required to induce resonance of the quartz oscillator, which is below several microwatts. The quartz oscillator does not require heating for detection, and therefore flammable hydrogen can be measured safely without temperature elevation. Another advantage is the small size of the quartz oscillator (1×4 mm), which allows its use in various locations, such as hydrogen storage, hydrogen stations, hydrogen transfer facilities, and fuel cell vehicles.

There are many demands on hydrogen sensing such as low detection limit (0.01 vol%), wide concentration range (1-100 vol%), safe, reliable and stable measurement on accuracy and sensitivity (<5%), fast response and recovery time (<1 s), low interference by other gases, low

sensitivity to environment of pressure (80-110 kPa), temperature (-30-80 °C) and humidity (10-98RH%), long lifetime (> 5 years), low power consumption (<100 mW) and cost (<100 euro per system), small size, simple operation and system integration and interface, and maintenance free (Hübert T. et al., 2011). Despite the variety of the hydrogen sensing methods, practical sensing methods that fulfill all of the requirements mentioned above have not been developed. From this viewpoint, hydrogen sensing using a quartz oscillator is one candidate as a practical hydrogen sensing method in the future hydrogen society because of its unique characteristics. Therefore, this chapter presents a review of novel hydrogen sensing methods using the quartz oscillator together with the test apparatus and procedures.

2. Principle for measurement

As mentioned in the Introduction, output from the quartz oscillator depends not only on the pressure but also on the viscosity and molecular weight of the measured gas. In this section, the correlation between the output from the quartz oscillator and the properties of the gas, such as viscosity and molecular weight, will be explained from a theoretical perspective. The output from the actual device used in this study will also be presented based on this explanation.

2.1. Theory for the quartz oscillator

The source for energy to the quartz oscillator is given by force from gas molecules hitting its surface. The electrical impedance of the quartz oscillator in the resonant state for gases can be described theoretically from the dissipation energy and the drag force (Kokubun K. et al., 1984). First, the electrical impedance Z can be expressed as follows.

$$Z = \frac{cV^2 \cos \theta}{A^2} \cdot f \quad (1)$$

Here, c , V , θ , A , and f are the constant, the constant supplied voltage, the phase difference between the voltage and current, the amplitude of the forced vibration, and the coefficient of the drag force between the surface of the quartz oscillator and the investigated gas, respectively. Equation (1) indicates that Z is proportional to f .

The drag force can be determined based on a string-of-beads model of the tuning-fork-shaped quartz oscillator. That is, the quartz oscillator is treated as a group of spherical objects. Using this "string of beads" model, the drag forces can be given by different formula depending on the nature of gas flow.

In the molecular flow region, where the mean free path of the gas molecules is sufficiently larger than the size of the spherical beads, the drag force is obtained from the kinetic theory as follows:

$$f = R^2 \sqrt{\frac{8\pi M}{R_0 T}} \cdot pu \quad (2)$$

Where R , M , p , u , R_0 , and T are the radius of the sphere, molecular weight, gas pressure, velocity, gas constant, and absolute temperature, respectively. As seen in equation (2), f is proportional to square root of M .

In the higher pressure region where the gas reaches viscous flow, the mean free path of the gas molecules is smaller than the size of the sphere and the gas medium can be regarded as a continuous fluid. Thus, the drag force can be calculated by fluid mechanics as follows:

$$f = 6\pi\eta R + \sqrt{2\eta\rho\omega} \quad (3)$$

Here, η , ρ , and ω are the coefficient of gas viscosity, density, and the angular frequency of the sphere, respectively. The formula of equation (3) means that the drag force in the viscous gas flow region is proportional to the square root of the product of the gas viscosity and the density.

Finally, from equations (1), (2), and (3), the expression on the impedance of the quartz oscillator can be summarized for the molecular and the viscous flow region as follows (Kokubun K. et al., 1987):

$$Z = CR^2 \sqrt{\frac{8\pi M}{R_0 T}} \cdot p \quad (4)$$

$$Z = C(6\pi\eta R + \sqrt{2\eta\rho\omega}) \quad (5)$$

where C is a constant. It should be noted that the density (ρ) can be rewritten as:

$$\rho = M \cdot p \quad (6)$$

By substituting equation (6) into equation (5), equation (5) can be converted as:

$$Z = 6\pi\eta R + \sqrt{2\eta M p \omega} \quad (7)$$

As above, in equations (4) and (7) it is clear that the electrical impedance of the quartz oscillator depends on the molecular weight in the molecular flow region and on the viscosity and the molecular weight of the measured gas in the viscous flow region, respectively. As the impedance of the quartz oscillator also depends on pressure, it must be pressure-calibrated to exclude the influence of pressure to obtain information on the properties of the measured gas. Finally, we can derive information on the viscosity and the molecular weight of the measured gas through this pressure-calibrated electrical impedance of the quartz oscillator.

2.2. Principle for hydrogen sensing

Normally, hydrogen sensing involves the detection of hydrogen that has leaked into air. Therefore, if a sensor can identify differences in gas properties between pure air and hydrogen-leaked air, it can be used for hydrogen sensing. As described in the previous

subsection, the electrical impedance of the quartz oscillator depends on the viscosity and molecular weight of the measured gas. The viscosity and molecular weight of hydrogen-leaked air will decrease compared to those of pure air because the values for hydrogen (8.35 $\mu\text{Pa s}$, 2.02) are smaller than those for air (17.08 $\mu\text{Pa s}$, 28.97), respectively (Golubev I. F., 1970). Therefore, measurement using the quartz oscillator can be used as a hydrogen sensing method because viscosity and molecular weight of the measured gas would change when hydrogen is leaked into air. In particular, the viscosity and molecular weight of hydrogen are markedly smaller than those of other gases, and therefore hydrogen can be detected with high sensitivity.

2.3. Principle for measurement of hydrogen concentration in air

One important advantage of hydrogen sensing with the quartz oscillator is the measurement of hydrogen concentration in air up to 100 vol% hydrogen. Hydrogen concentration can be measured by application of partial pressure measurement to binary gas mixtures (Kurokawa A. et al., 2004; Suzuki A. and Nonaka H., 2008). This partial pressure measurement can measure the partial pressures of each gas because viscosity and molecular weight of binary gas mixtures are only dependent on the composition ratio of each gas. Average molecular weight of binary gases depends on and changes monotonically with the partial pressure ratio. Therefore, if viscosity of binary gases changes monotonically with partial pressure ratio, the viscosity of binary gas mixtures determines the partial pressure ratio. In the case of binary gas mixtures, the partial pressure ratio determines the partial pressures of each gas, and thus the partial pressure can be measured for binary gases.

Hydrogen concentration in air can be measured if hydrogen-leaked air is assumed to be a binary gas mixture of hydrogen and air. Of course, air itself is also composed of multiple gases, but it can be treated as a single kind of gas with constant viscosity and molecular weight because the kinds and densities of gases in air are normally constant.

As mentioned above, the quartz oscillator can be used to measure hydrogen concentration up to 100 vol% if viscosity of the binary gas mixtures changes with the partial pressure ratio without any saturation of output from the hydrogen sensor as seen in chemical hydrogen sensors.

3. Experimental setup

Figure 1 shows the experimental setup used in this study, consisting of a vacuum chamber, gas supply, and equipment for data processing (Suzuki A. et al., 2006). The main vacuum chamber was a 90-cm³ stainless steel tube, where the quartz friction pressure gauge (VP Co. model GC-210) including the quartz oscillator and a diaphragm gauge (MKS Instruments, Baratron model 222BA) were fixed. Outputs from the gauges, temperature, and the signals from gas valves were sent to a digital multimeter and analyzed on a personal computer. Gas inlet and position of the quartz oscillator depended on the type of test. Therefore, they will be presented in the following section as well as details of the quartz friction pressure gauge and the quartz oscillator. Figure 2 shows the quartz oscillator and quartz friction pressure

gauge. The part of the left hand side where the quartz oscillator is fixed is included in the right hand side of the quartz friction pressure gauge. It should be noted that the size of the connection plug at the quartz friction pressure gauge is 3/8". The size of the quartz oscillator is less than 1 × 4 mm.

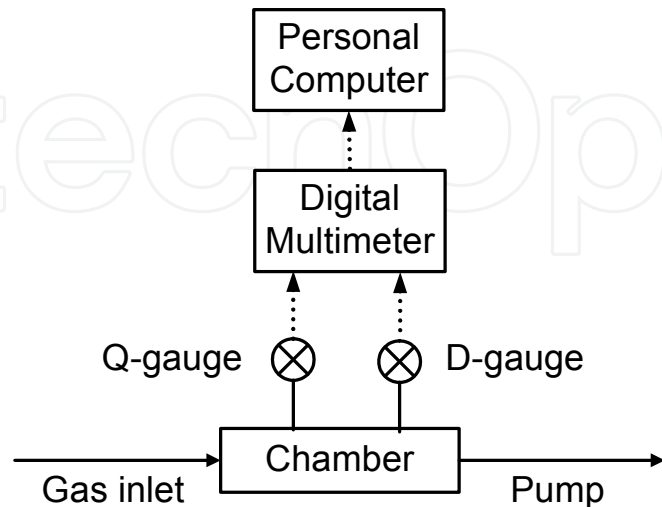


Figure 1. Schematic diagram for experimental setup: Q-gauge: quartz friction pressure gauge; D-gauge: diaphragm pressure gauge

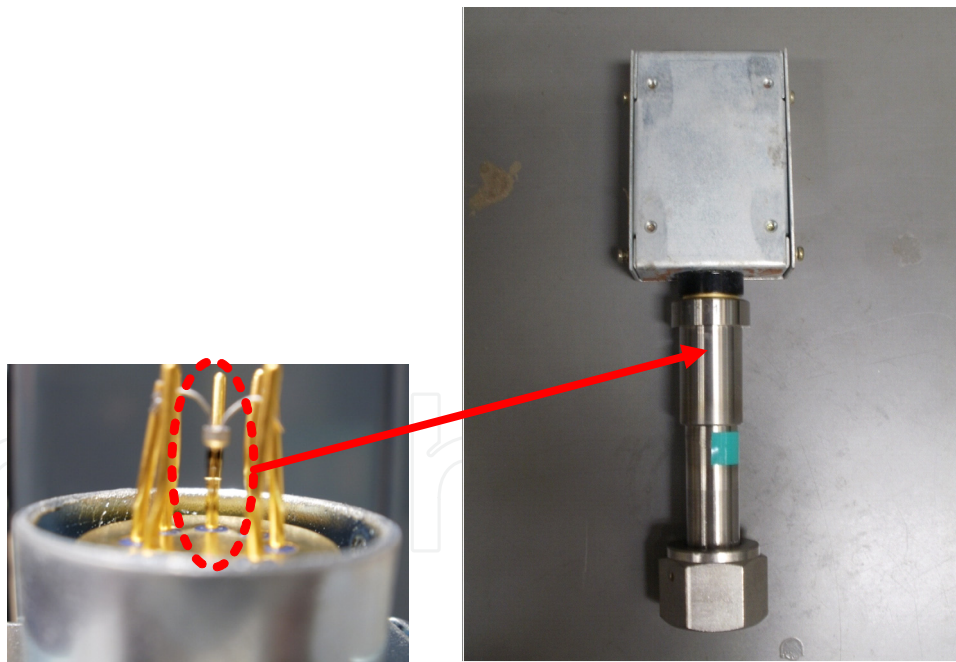


Figure 2. (Outlook) image of the quartz oscillaor (left) and the quartz friction pressure gauge (right)

3.1. Output from the quartz oscillator based on the electrical impedance

The electrical impedance of the quartz oscillator mentioned in Section 2.1 is difficult to measure experimentally. Instead, the voltage was obtained by measuring the current of the quartz oscillator for simplicity (Ono M. et al., 1985).

Pressure dependence of the impedance-converted-voltage in the pressure range up to 100 kPa was investigated for air in Figure 3. The inset in Figure 3 shows the results for the range up to 0.3 kPa. The impedance-converted-voltage decreased with pressure when measured for one kind of gas, but depended on the kinds of measured gas because the electrical impedance of the quartz oscillator depends on viscosity and molecular weight of the measured gas as discussed in Section 2.1.

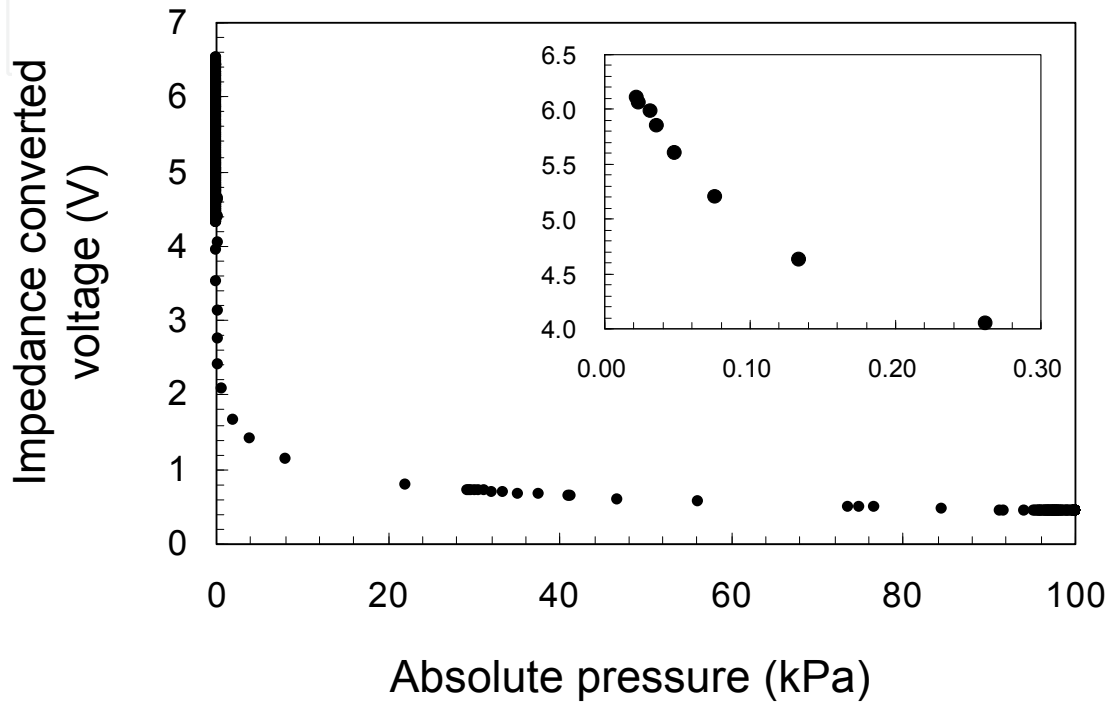


Figure 3. Pressure dependence of impedance-converted-voltage measured for air

One advantage of the quartz oscillator for pressure measurement shown in Figure 3 is wide range pressure measurement of 0.01-100 kPa with one gauge. This almost five orders of magnitude range of pressure measurement is useful because such pressures can be measured with one pressure gauge. In fact, such a pressure gauge applicable to the pressure range of 0.01-100 kPa has been developed (Kobayashi T. et al., 1996; Ono M. et al., 1985). Details of this gauge are presented in the following subsection.

3.2. Pressure readings from quartz friction pressure gauge

The pressure gauge with the quartz oscillator is named the “quartz friction pressure gauge” (Ono M. et al., 1985). The pressure reading from this quartz friction pressure gauge is derived from the impedance-converted-voltage through pressure calculation (Kokubun K. et al., 1987). The calculation is based on equations (4) and (7) depending on the nature of gas flow. The pressure around the border between the molecular and viscous flow region was obtained by fitting of equations (4) and (7) to the experimental results (Kokubun K. et al., 1987). It should be noted that the pressure reading from the quartz friction pressure gauge

depends on the kinds of gas measured because the electrical impedance of the quartz oscillator, which is the source for the pressure reading, depends on the viscosity and molecular weight of the measured gas. The pressure reading from the quartz friction pressure gauge is originally not absolute pressure, but a nominal pressure. By introducing the gas-dependent-constant, the pressure reading can be the absolute pressure for the measured gas.

This nominal pressure mentioned above measured for air is plotted against the absolute pressure in Figure 4. The absolute pressure was measured with a diaphragm gauge presented in Figure 1. Here, the kind of gas is set to air for the quartz friction pressure gauge, and therefore the pressure reading from the quartz friction pressure gauge mostly agrees with absolute pressure.

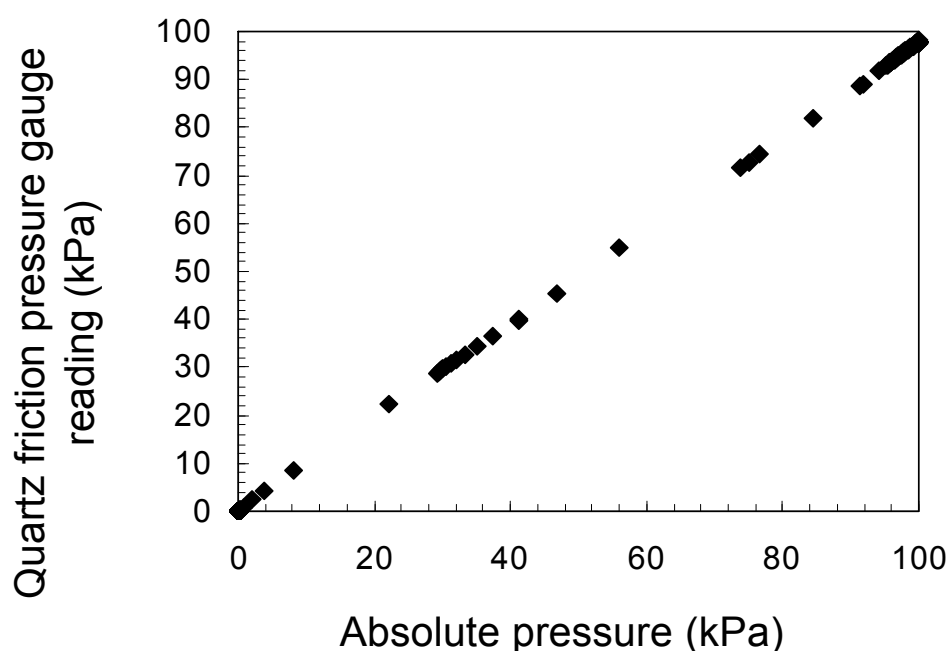


Figure 4. Absolute pressure dependence of pressure reading from quartz friction pressure gauge measured for air

4. Hydrogen sensing with the quartz friction pressure gauge

The characteristics of hydrogen sensing with the quartz oscillator were investigated using the quartz friction pressure gauge shown in Figure 2. The quartz friction pressure gauge generates output in the form of nominal pressure, but it is sufficient to determine the capability for hydrogen sensing.

4.1. Hydrogen sensing in hydrogen-leaked air

For preliminary tests, atmospheric air and hydrogen were introduced into the chamber with the quartz friction pressure gauge (Suzuki A. et al., 2006). Figure 5 shows a schematic

diagram of the chamber and gas introduction. Air was introduced into the chamber with the quartz friction pressure gauge and a diaphragm gauge from atmospheric air without any purification. On the other hand, hydrogen was introduced into the chamber through a mass flow controller to control hydrogen concentration. This method of gas introduction is similar to hydrogen leakage into atmospheric air, and therefore this test should be practical.

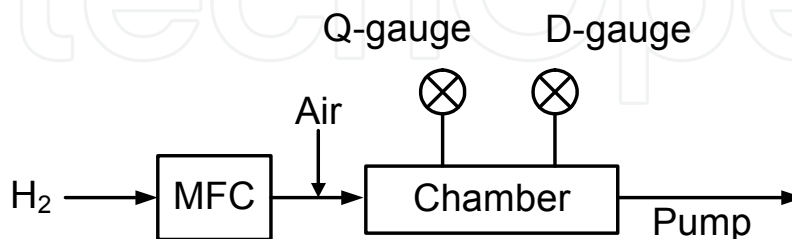


Figure 5. Experimental setup for test on hydrogen-leakage detection with the quartz friction pressure gauge; MFC: mass flow controller

The pressure readings of the quartz friction and the diaphragm pressure gauges when hydrogen was introduced into the vacuum chamber and terminated are shown in Figure 6. At the beginning, when only atmospheric air was introduced into the vacuum chamber, both the quartz friction gauge and the diaphragm pressure gauge readings were equal. This is reasonable because the quartz friction pressure gauge reading is calibrated for air. About 10 minutes later, 70 sccm of hydrogen gas was introduced into the vacuum chamber, and the quartz friction pressure gauge readings decreased markedly, while the diaphragm pressure gauge reading remained constant¹. After about 35 minutes, the quartz friction pressure gauge reading reached a constant value. After saturation of the quartz friction pressure reading, introduction of hydrogen into the vacuum chamber was interrupted. The quartz friction pressure gauge reading began to return to the value before the introduction of hydrogen.

As there were almost no changes in the diaphragm pressure gauge reading, the change in quartz friction pressure gauge reading at the commencement and termination of hydrogen introduction do not result from changes in absolute pressure. Therefore, these changes in quartz friction pressure gauge reading must be attributable to the differences in viscosity and molecular weight between hydrogen-leaked and pure air. This quartz friction pressure gauge reading is proportional to the viscosity of the measured gas and calibrated as air. Introduction of low viscosity and molecular weight hydrogen into air reduced the viscosity and molecular weight of hydrogen-leaked air and resulted in a decrease in the quartz friction pressure gauge reading. After termination of hydrogen introduction, the hydrogen-leaked air was replaced by pure air, and therefore the viscosity and molecular weight of the measured gas and the quartz friction pressure gauge reading returned to the earlier values.

¹ Flow rate in m³ caribrated at 1.103x10⁵ Pa and 273 K

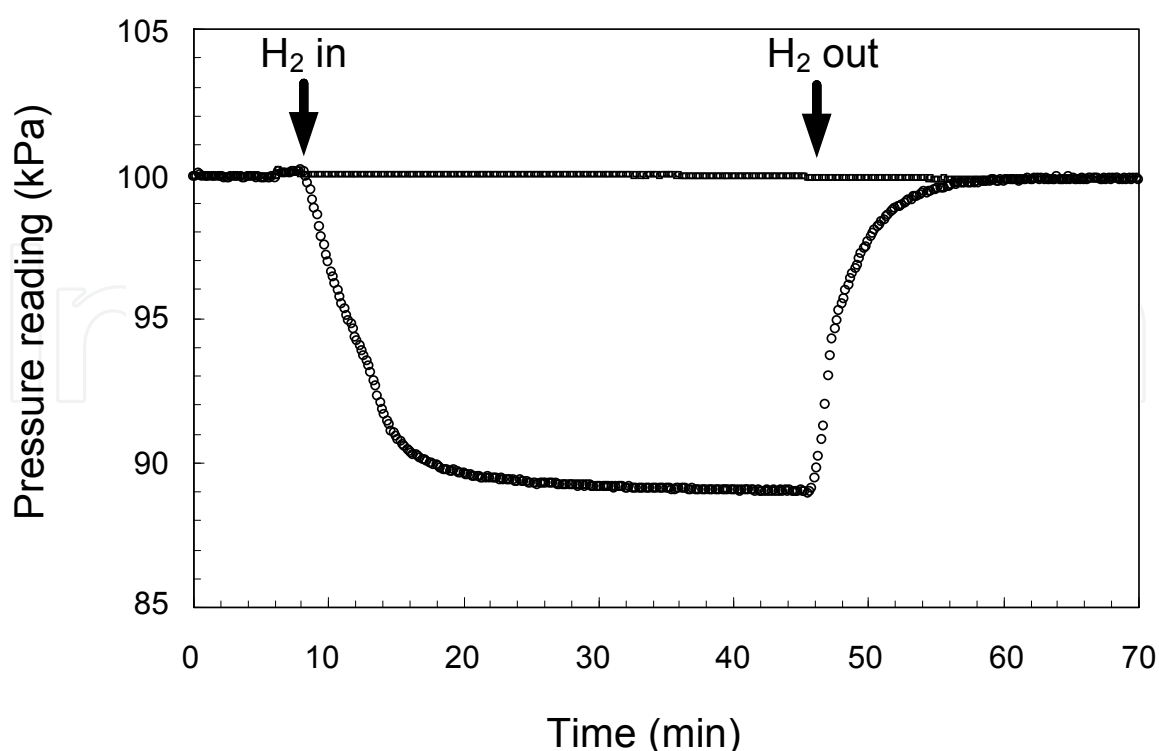


Figure 6. Temporal change of pressure readings of the quartz friction (circle) and diaphragm (square) pressure gauges

4.2. Long-term detection of hydrogen leakage into air

Hydrogen sensing normally must be used and work 24 h per day. To investigate the repeatability of hydrogen sensing using the quartz friction pressure gauge and hydrogen gas flow dependence, the long-term hydrogen sensing was tested. The results of long-term range hydrogen sensing are shown in Figure 7. Arrows and numbers at the top of Figure 7 a) indicate the time at which hydrogen was introduced and the flow rates in sccm, respectively.

Figure 7 a) shows the time-evolution of quartz friction and the diaphragm pressure gauge readings when hydrogen was introduced and interrupted several times with different flow rates. For almost all times in a day, the quartz friction pressure gauge reading decreased with introduction of hydrogen and returned with its termination, indicating that the repeatability of hydrogen sensing with the quartz friction pressure gauge is reliable.

Figure 7 b) shows the pressure-calibrated quartz friction pressure gauge reading ratio with hydrogen introduction and termination. The pressure-calibration of the quartz friction pressure gauge readings was carried out by dividing the quartz friction pressure gauge readings by absolute pressure measured with the diaphragm pressure gauge. The diaphragm pressure gauge reading was also normalized with the initial pressure with $t=0$ to determine the temporal changes in atmospheric pressure. It is clear that the pressure-calibrated quartz friction pressure gauge reading ratio responded to hydrogen introduction and termination in Figure 7 b) as well as in Figure 7 a), even if the atmospheric pressure

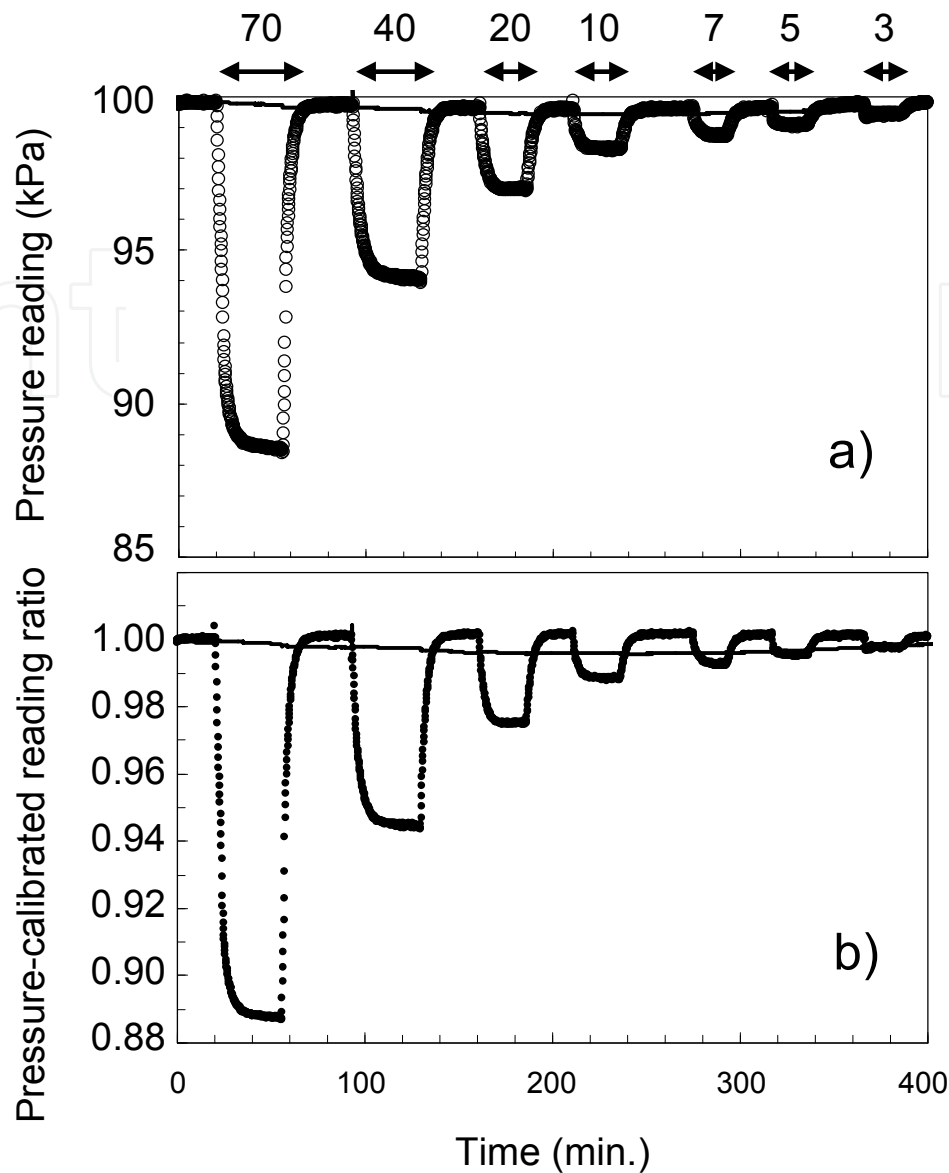


Figure 7. Temporal change of pressure readings of the quartz friction (circle) and diaphragm (line) pressure gauges a) and the pressure-normalized quartz friction (dot) and the initial pressure-normalized pressure readings for hydrogen introduction and termination b).

fluctuated. Therefore, this method was shown to be practical for long-time hydrogen sensing using the pressure-calibrated quartz friction pressure gauge reading ratio although the atmospheric pressure fluctuated.

Both raw and pressure-calibrated quartz friction pressure gauge readings during hydrogen introduction depended on the introduced hydrogen flow rates. This pressure-calibrated quartz friction pressure gauge reading ratio should only depend on viscosity and molecular weight of the measured gas because the influence of pressure was excluded. Therefore, the results shown in Figures 7 a) and b) indicate the possibility of measurement of hydrogen concentration in hydrogen-leaked air using this pressure-calibrated quartz friction pressure gauge reading ratio.

4.3. Hydrogen concentration measurement with quartz friction pressure gauge

The hydrogen concentration dependence of the pressure-calibrated quartz friction pressure gauge reading at a total pressure of 100 kPa was investigated to measure hydrogen concentration in hydrogen-air gas mixtures based on the partial pressure measurement for binary gas mixtures described in the Introduction. For this purpose, gas mixtures containing known hydrogen concentrations in air must be prepared using the experimental setup in Figure 8 and the following procedure.

Known concentrations of hydrogen in hydrogen-air gas mixtures were prepared based on the diaphragm pressure reading. One example of this diaphragm pressure gauge reading during preparation of hydrogen-air gas mixtures with known hydrogen concentration is plotted in Figure 9 to explain the procedure for preparing hydrogen-air gas mixtures with 10 vol% hydrogen and 100 kPa total pressure. First, the pressure in the vacuum chamber was zero. Then, at $t=9$ min for this case, hydrogen was introduced into the chamber until the diaphragm pressure gauge reading reached 10 kPa with shutting the vacuum pump by closing a valve on the vacuum pump. This means that the chamber contained 10 kPa hydrogen. Next, air was introduced into the chamber at $t=22$ min in this case until the diaphragm pressure gauge reading reached 100 kPa, meaning that the chamber contained (100-10) kPa air. Finally, 10 vol% = 10 kPa/(10+90) kPa hydrogen and total pressure of 100 kPa hydrogen-air gas mixture was prepared in the chamber.

The quartz friction pressure gauge reading at $t=40$ min in Figure 9 for 100 kPa and 10 vol% hydrogen-air gas mixture was about 95 kPa. Other hydrogen-air gas mixtures with known hydrogen concentrations were also prepared in the same way as described above. Finally, the hydrogen concentration dependence of the pressure-calibrated quartz friction pressure gauge reading ratio is summarized in Figure 10. The results indicated that the pressure-calibrated quartz friction pressure gauge reading ratio depends on hydrogen concentration in hydrogen-air gas mixtures at 100 kPa. Here, the pressure-calibrated quartz friction pressure gauge reading ratio was used instead of raw quartz friction pressure gauge readings to eliminate the effect of pressure difference for each gas mixture. Using Figure 10, the hydrogen concentration in hydrogen-air gas mixtures can be determined by measurements using a quartz friction gauge and a diaphragm pressure gauge.

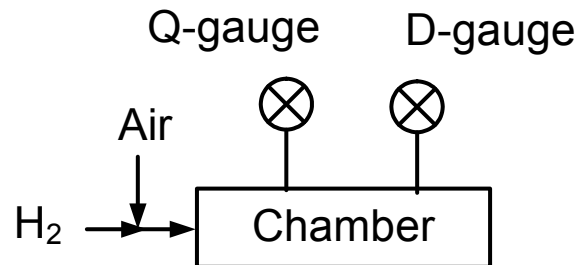


Figure 8. Experimental setup for preparation for the hydrogen-air gas mixtures with known concentration hydrogen

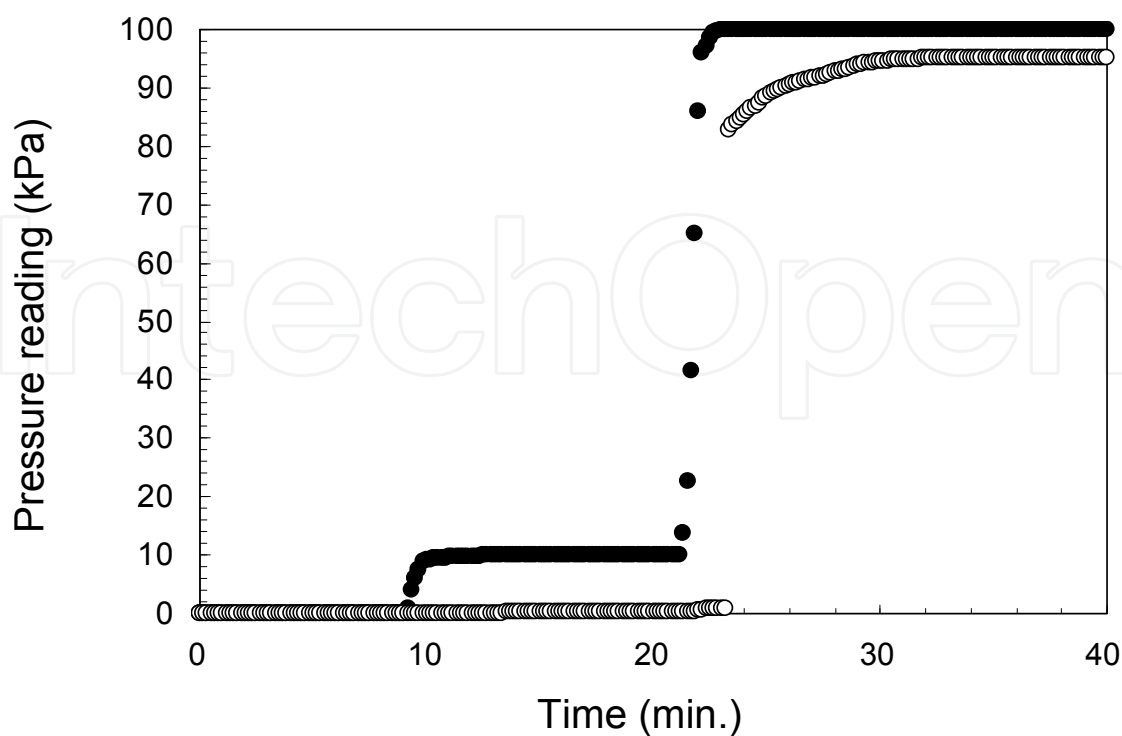


Figure 9. Diaphragm (closed) and quartz friction (open) pressure gauge reading during preparation for the 100 kPa hydrogen-air gas mixtures with 10vol.% hydrogen

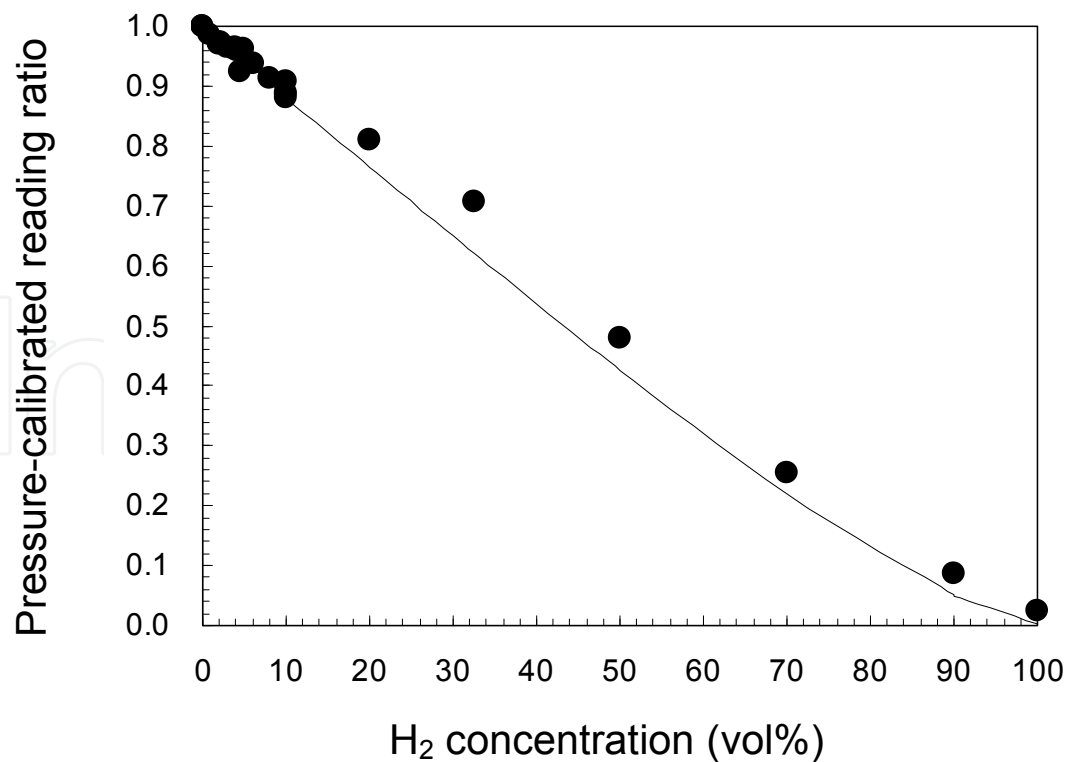


Figure 10. Hydrogen concentration dependence of the pressure-calibrated quattz friction pressure gauge reading ratios

To understand this hydrogen concentration dependence of the pressure-calibrated quartz friction pressure gauge reading ratio, we discuss the viscosity of gas mixtures based on a previous report by Wilke because the reading depends on the viscosity of the measured gas, as seen in equation (7) presented in Section 2.1 (Wilke C. R., 1950). Based on Wilke's work, the viscosity of binary gas mixtures (η_m) can be written as follows:

$$\eta_m = \sum_{i=1}^2 \frac{\eta_i}{1 + \frac{1}{x_i} \sum_{\substack{j=1 \\ j \neq i}}^2 x_j \phi_{ij}} \quad (8)$$

Here, η and x are viscosity and fraction of each gas in the binary gas mixtures. In addition, ϕ is given by

$$\phi_{ij} = \frac{[1 + (\eta_i / \eta_j)^{1/2} (M_j / M_i)^{1/4}]^2}{(4 / \sqrt{2}) [1 + (M_i / M_j)]^{1/2}} \dots \quad (9)$$

where M is the molecular weight of each gas. By assuming viscosity at 0 and 100 vol% hydrogen concentration as those of pure air and hydrogen, respectively, equation (8) is expressed by the line in Figure 10, which agrees well with the pressure-calibrated quartz friction pressure gauge reading ratio and indicates the viscosity of the hydrogen-air gas mixture.

From differences in the pressure-calibrated quartz friction pressure gauge readings of 0.024 and 1.0 between 0 and 100 vol% hydrogen concentration and its fluctuation of 0.001, the minimum detectable hydrogen concentration is derived as $(1.0-0.024)/100/0.001=0.1\text{vol\%}$, which is sufficiently low for practical hydrogen sensing (DOE, 2007)

4.4. Response and recovery time measurement for hydrogen sensing

As shown in Figure 6, the response time for hydrogen introduction, which is defined as the time to reach 90% of saturated readings, seems to be on the order of several minutes. However, this is not because of intrinsic characteristics of the quartz friction pressure gauge but due to the slow introduction of hydrogen. Therefore, the response and recovery time for hydrogen introduction and termination were measured using combined valves with which the gas flow can be quickly switched.

Temporal changes in the pressure calibrated quartz friction and the diaphragm pressure gauge reading ratios and signals for 1 vol% hydrogen introduction and termination using quick gas switching are shown in Figure 11 (Suzuki A. et al., 2006). From Figure 11, it is clear that the response and recovery times for hydrogen introduction and termination were below 1 s (about 600 ms). This response and recovery times also fulfilled the requirements for hydrogen sensing.

It should be noted that these response and recovery times were independent of hydrogen concentration, as indicated in Figure 12, which shows the temporal changes in the quartz

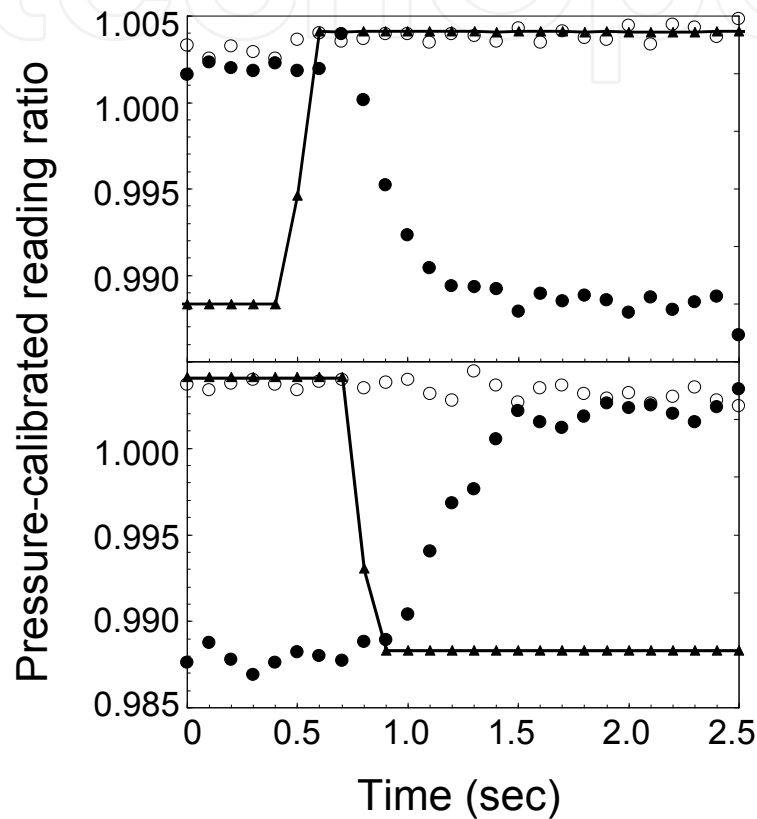


Figure 11. Temporal changes in the pressure calibrated quartz friction (closed) and the diaphragm (open) pressure gauge reading ratios and signal for hydrogen introduction and termination (triangle)

friction pressure gauge reading for various hydrogen concentrations for hydrogen introduction and termination. Figure 13 summarizes the hydrogen concentration dependence of response and recovery times, indicating values below 1 s even for higher hydrogen concentrations. Thus, the quartz friction pressure gauge can be used to measure hydrogen concentration as quickly as hydrogen-leakage detection. This simultaneous hydrogen concentration measurement will be useful with regard to safety.

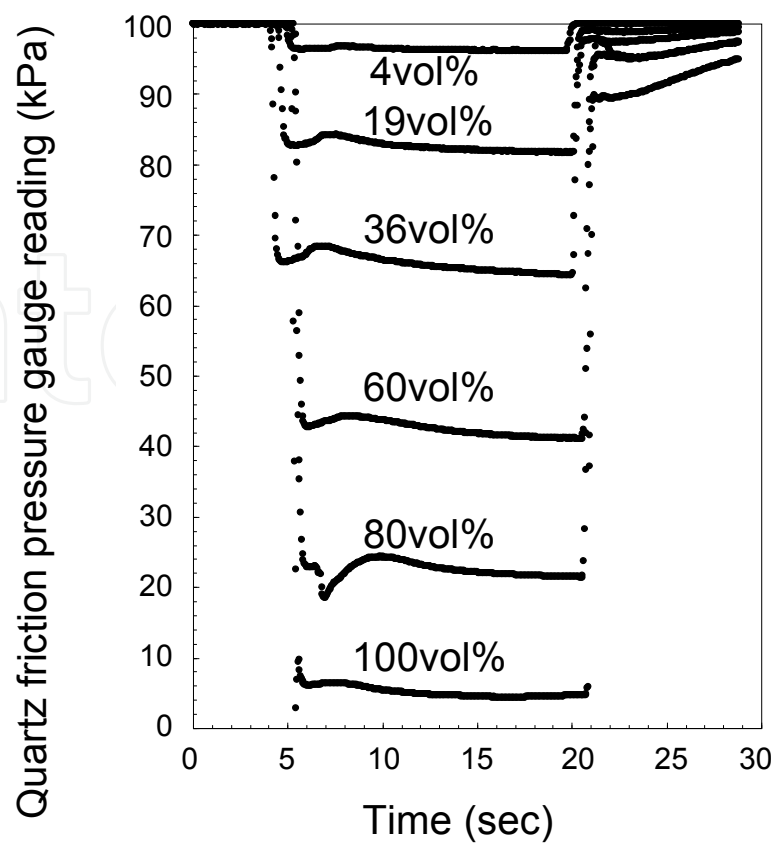


Figure 12. Temporal changes in the pressure-calibrated quartz friction pressure gauge readings for various hydrogen concentration (in vol%)

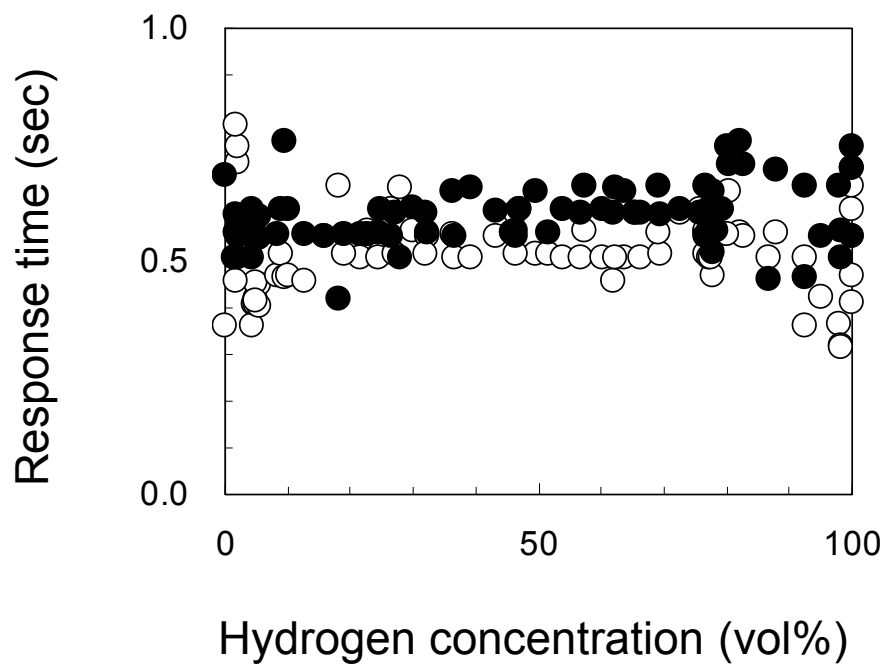


Figure 13. Response time to the hydrogen introduction (open) and recovery time (closed) for 0.1-100vol% hydrogen concentration

4.5. Influences of temperature and humidity

As hydrogen sensors are used outside, the influences of temperature and humidity on hydrogen sensing with the quartz friction pressure gauge were investigated. In this study, the influences on background of the quartz friction pressure readings without hydrogen were investigated. The resonant frequency of the quartz oscillator, which affects the electrical impedance of the quartz oscillator and the quartz friction pressure gauge readings, is dependent on temperature (Spasov L. et al., 1997). Humidity should also affect the quartz friction pressure gauge reading because viscosity and molecular weight of water ($12.55 \mu\text{Pa s}$, 18.02), which is the source of humidity, are smaller than those of air.

Figures 14 and 15 show the temperature and humidity dependences of the pressure-calibrated quartz friction pressure gauge reading ratio, respectively. At constant humidity and temperature, the pressure-calibrated quartz friction pressure gauge reading ratios depends on temperature and humidity. The changes in pressure-calibrated reading ratio between 22°C and 34°C in Figure 14 and between 37% and 100% relative humidity (RH) in Figure 15 correspond to 0.36 and 1.74 vol\% hydrogen in atmospheric air, respectively.

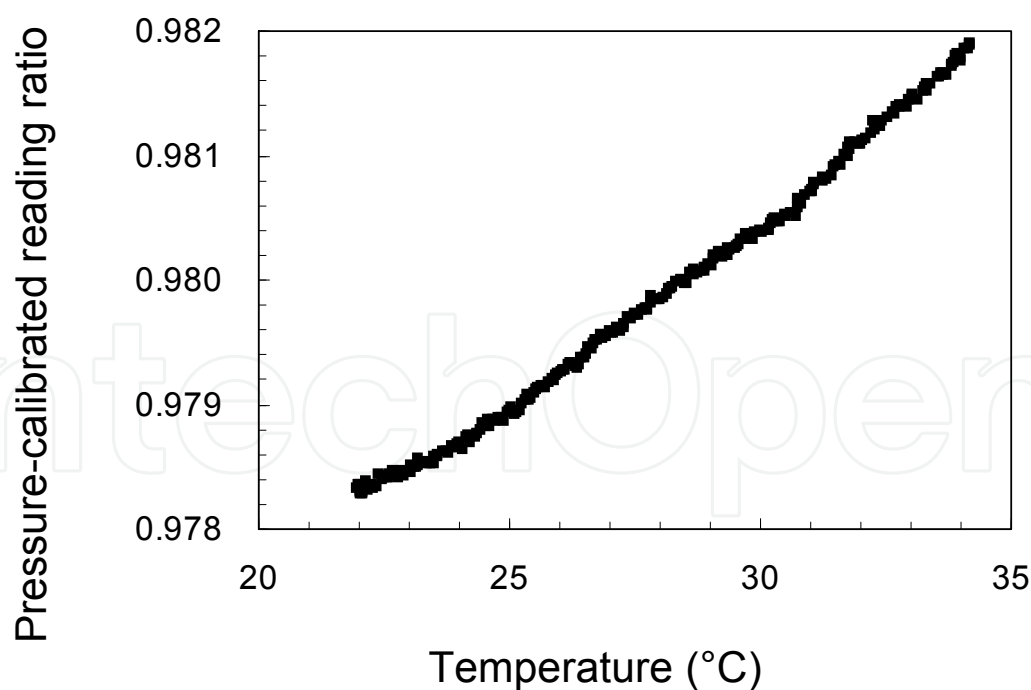


Figure 14. Temperature dependence of pressure-calibrated quartz friction pressure gauge reading ratio at 30% relative humidity

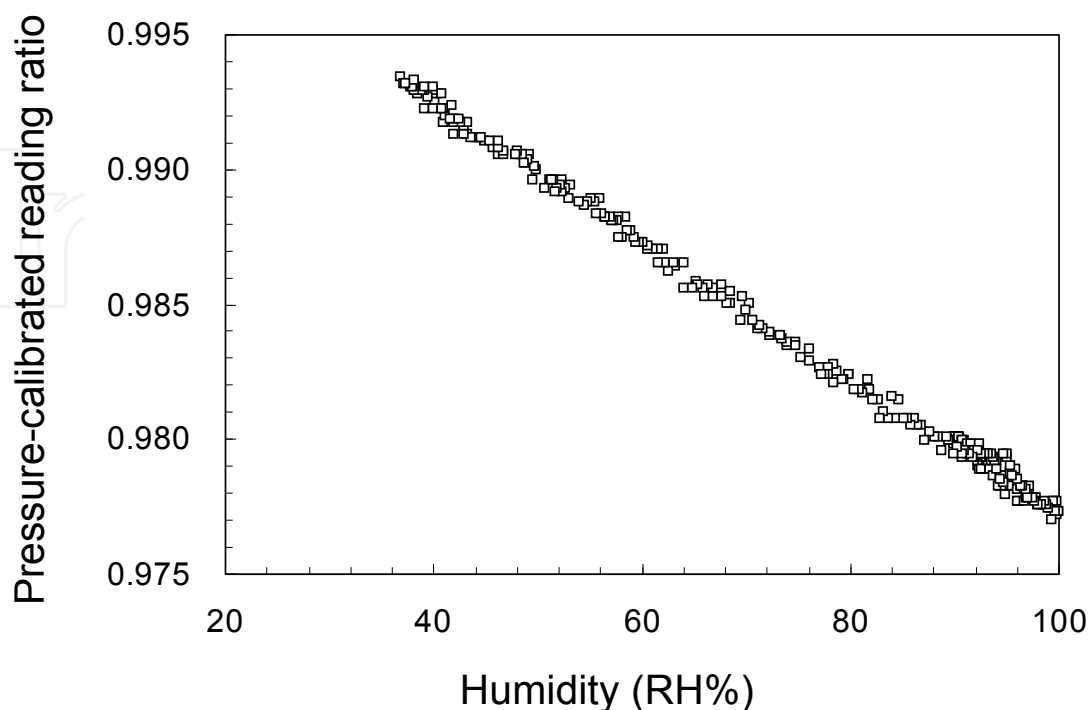


Figure 15. Relative humidity dependence of pressure-calibrated quartz friction pressure gauge reading ratio at 32.5 °C

A hydrogen concentration of 1.74 vol% is greater than the lower explosion limit, and therefore this change induced by humidity may cause errors in hydrogen sensing, and must be avoided.

These influences can be excluded by measuring temperature and humidity at the same time. By calibrating the pressure-calibrated reading ratio using temperature and humidity dependence, these influences can be reduced down to 0.005, corresponding to 0.5 vol% hydrogen and is below lower explosion limit. However, further improvements are required because it is necessary to better suppress the influences of temperature and humidity and the present calibration procedure and measurement apparatus are complicated.

4.6. Interference by other gases

There are two possible types of gas that can interfere with hydrogen sensing using the quartz friction pressure gauge. The first is gas that can directly cause deterioration of the quartz itself, such as fluorinated gases. The other type of interfering gas significantly affects viscosity and molecular weight of the measured gas. One such gas was already mentioned as humidity, i.e., water. From this viewpoint, helium would have the greatest effect because its viscosity and molecular weight (18.60 μ Pa s, 4.00) are as small and are similar to those of hydrogen. Leakage of helium into air would reduce the quartz friction pressure gauge reading to almost the same extent as hydrogen leakage (A. Suzuki and H. Nonaka, 2008).

5. Conclusions

The present specifications of hydrogen sensing using the quartz friction pressure gauge are summarized in Table I. Almost all specifications meet the requirements for hydrogen sensing. Therefore, it can be concluded that hydrogen sensing using the methods described here is sufficiently practical for the hydrogen society.

Measurement range	0.1-100 vol%
Operating temperature	15°C-40°C
Response time	< 1.0 s
Accuracy	0.5%
Gas environment	Ambient air, 0%-90% relative humidity range
Interference resistive	Helium, water (humidity)
Sensor head size	1 × 4 mm
Power	Microwatts

Table 1. Present specifications of hydrogen sensing with the quartz friction pressure gauge

6. Future research

Several problems remain for the practical use of hydrogen sensing using the quartz friction pressure gauge as follows.

6.1. Reduction of influences of temperature and humidity

The most serious problem for hydrogen sensing with the quartz friction pressure gauge is the requirement of suppressing the influences of temperature and humidity when used outside. Solutions to these problems may be as follows.

6.1.1. Reduction of the influence of temperature

The resonant frequency of the quartz oscillator depends on temperature. Therefore, the quartz friction pressure gauge reading can be temperature-calibrated using the resonant frequency. This can be applied to hydrogen sensing with the quartz friction pressure gauge.

6.1.2. Reduction of the influence of humidity

To reduce the influence of humidity, some filters may be effective to prevent water coming into contact with the head of the quartz friction pressure gauge. Such effects must be studied with varying humidity and hydrogen concentration simultaneously.

6.2. Improvement of sensitivity for hydrogen sensing

The quartz friction pressure gauge reading is calculated with the digitized electrical impedance of the quartz oscillator. Analog-digital conversion of the electrical impedance of

the quartz oscillator reduces the resolution from 24 to 8 bit. In addition, pressure calculation also includes about 10% deviation because of the approximation for the pressure derivation. Therefore, use of the electrical impedance of the quartz oscillator may reduce the minimum detection concentration of hydrogen by skipping these inaccurate processes.

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